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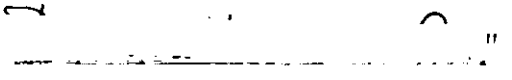


STRUCTURES OF PHOTOCHEMICAL ADDUCTS OF MALEIC ANHYDRIDE WITH BENZENE, TOLUENE, AND *p*-XYLENE

A THESIS

Presented to

the Faculty of the Graduate Division

by

Durvasula Visweswara Rao

In Partial Fulfillment

of the Requirements for the Degree

Master of Science in Chemistry

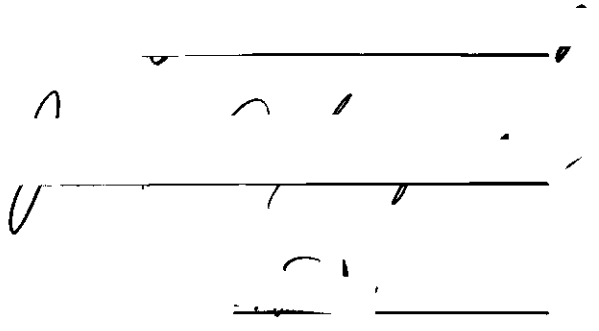
Georgia Institute of Technology

March, 1961

STRUCTURES OF PHOTOCHEMICAL ADDUCTS OF MALEIC ANHYDRIDE

WITH BENZENE, TOLUENE, AND p-XYLENE

Approved:



Date Approved by Chairman:

January 31, 1961

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He is grateful to his parents for their support and encouragement during this period of graduate work.

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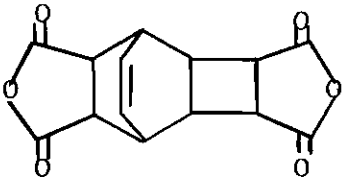
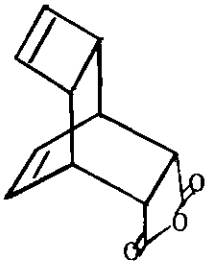
SUMMARY

It was found that benzene combines with two molecules of maleic anhydride under the influence of ultraviolet light to give a white crystalline adduct which is assigned the structure:

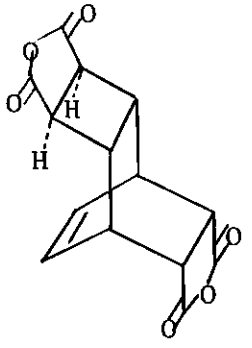


This structure assignment rests in part upon oxidation of the adduct with lead tetraacetate in pyridine to give a product which is identical with the known maleic anhydride addition product of cyclöoctatetraene. This maleic anhydride addition product of cyclöoctatetraene is assigned the stereochemical formula:



This assignment was made on the basis that it forms a bromo γ-lactone before and after partial hydrogenation, and from the previously known fact that it forms a crystalline rhodium(I) chloride complex.

From these and other observations the stereochemical structure of the adduct obtained by irradiation of a solution of maleic anhydride in benzene appears to be:



A solution of maleic anhydride in toluene on irradiation gave a liquid adduct from which a crystalline product was isolated and characterized as benzylsuccinic acid. The remaining liquid fraction after esterification appears to be a complex mixture on the basis of its vapor-phase chromatogram.

p-Xylene also reacts with maleic anhydride in presence of ultraviolet light to give a liquid adduct. From the liquid adduct was isolated a crystalline product which was characterized as p-methylbenzylsuccinic acid. From the remaining liquid portion, after esterification, purification by vacuum distillation and then on saponification there was obtained a crystalline product which was characterized also as p-methylbenzylsuccinic acid.

CHAPTER I

INTRODUCTION

The absorption of ultraviolet and visible light causes electronic excitation in organic molecules. The magnitude of the excitation may vary from ten to hundreds of kilocalories in accordance with Einstein's equation (the intense line of 2537.5 A from the mercury vapor lamp corresponds to 112.62 kcal./mole). The absorbed energy may be dissipated as heat, by phosphorscence, or by fluorescence. Alternatively, the energy may lead to bond breaking or bond making. Photochemical activation may lead to new organic molecules. The literature on photochemical reactions has been surveyed in three recent books (I). In the present chapter some photochemical additions of multiple bonds to other multiple bonds will be reviewed along with some related work. For brevity, reactions which have been reviewed by Taylor(2) will not, in general, be considered further here.

There are several cases where photochemical dimerizations have been achieved. An interesting example is the formation of a dimer

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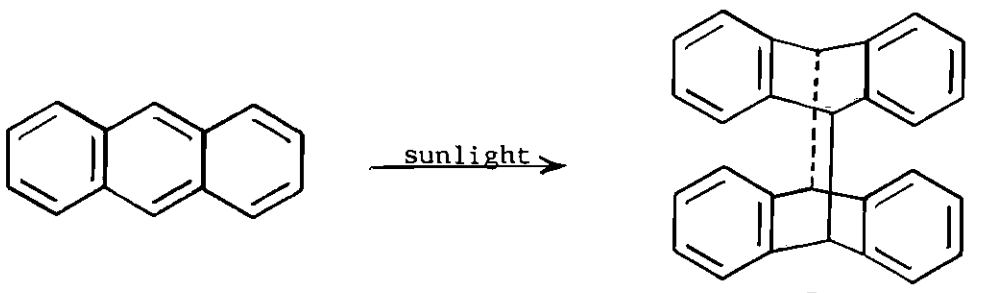
(1) C. R. Mason, V. Boekelheide, and W. Albert Noyes, Jr., "Photochemical Reactions". in A. Weissberger, ed., Techniques of Organic Chemistry, Vol. II, Interscience Publishers, Inc., New York, N. Y., 1956. pp. 257-384; A. Schönberg, Preparative Organische Photochemie, Springer-Verlag, Berlin, 1958; C. Walling, Free Radicals in Solutions, J. Wiley and Sons, Inc., New York, N. Y., 1957. pp. 539-558.

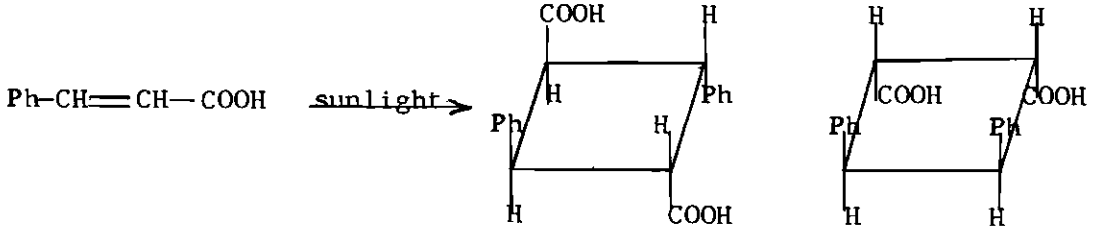
(2) J. W. Taylor, Photochemically Induced Reactions of Benzene with Maleic Anhydride, Part II, unpublished M. S. Thesis, Georgia Institute of Technology, 1958, pp. 25-27.

(I) when anthracene is exposed to sunlight(3).



I

Certain ethylenic compounds when irradiated in the solid state undergo dimerization to form cyclobutane derivatives(4). For example, cinnamic acid in sunlight yields the isomeric truxillic (II) and truxinic acids (III)(5).



II III

Dimethyl fumarate also undergoes dimerization in the solid state upon irradiation with ultraviolet light to give 1,2,3,4-tetracarbomethoxy-

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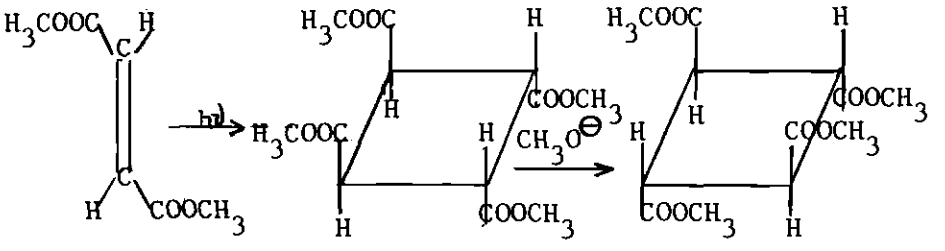
(3) F. D. Green, S. L. Misrock, and J. R. Wolfe, J. Am. Chem. Soc., 77, 3852 (1955); see also C. A. Coulson, L. E. Orgel, W. Taylor, and J. Weiss, J. Chem. Soc., 2961 (1955).

(4) See A. Mustafa, Chem. Revs., 51, 1 (1952) for a review.

(5) H. I. Bernstein and W. C. Quimby, J. Am. Chem. Soc., 65, 1845 (1943).

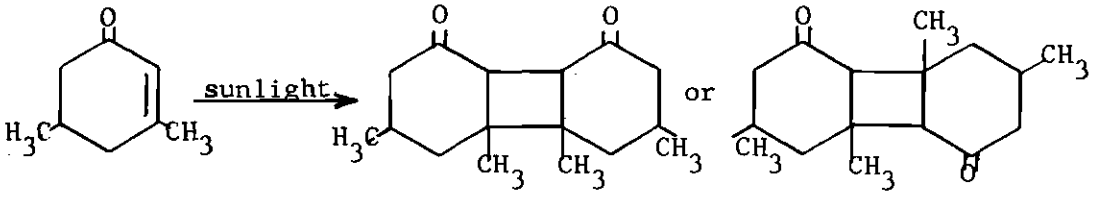
cyclobutane(6) of stereochemical structure (IV). Treatment of (IV) with sodium methoxide in methanol effects stereochemical equilibration and leads to an ester which has been assigned an all <u>trans</u> structure (V).



IV V

Irradiation of fumaronitrile also gives a product which after hydrolysis with hydrogen chloride in acetic acid and esterification with diazomethane is found to be identical with the ester (IV)(6).

Dimerizations of this nature may involve a double bond which is part of a ring system(4). Many such reactions occur in solution. For example, 3,5-dimethylcyclohex-2-enone (VI) in alcoholic solution yields a photodimer (VII) on exposure to sunlight(7).



VI VIIa VIIb

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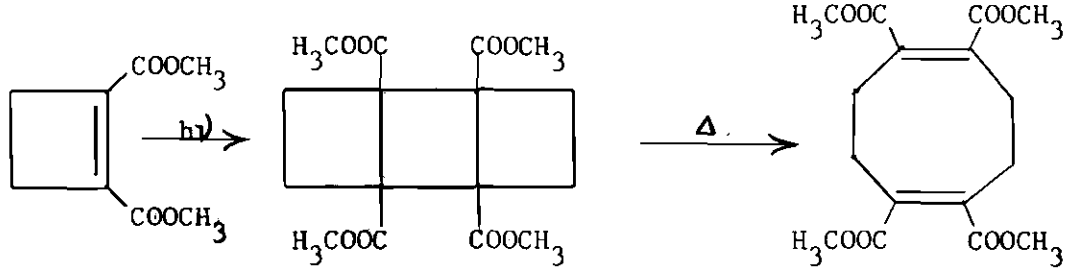
(6) W. Griffin, J. E. Basinski, and A. F. Vellturo, <u>Tetrahedron Letters</u>, <u>No. 3</u>, 13 (1960).

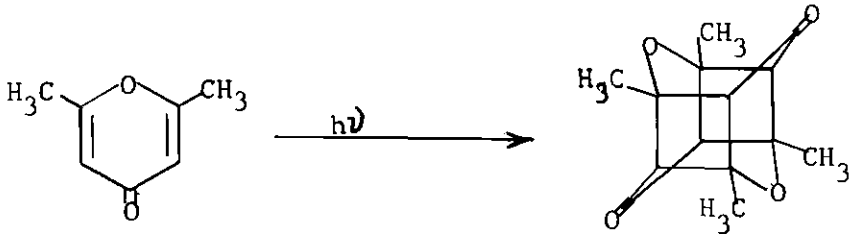
(7) W. Triebs, <u>J. Prakt. Chem.</u>, <u>138</u>, 299 (1933).

The dimethylcyclobutene-1,2-dicarboxylate of structure (VIII) has been reported to give a dimer (IX) on irradiation(8). The dimer on heating gives rise to a cyclooctadiene derivative(8).



VIII IX X

A very interesting photodimer (XI) with a cage structure has been reported(9) on irradiating solid 2,6-dimethyl-4-pyrone with ultraviolet light.



XI

On exposure to ultraviolet light, solid 2,5-dimethylbenzoquinone forms a colorless photodimer (XII)(10). Structure (XII) has been assigned since the dimethylbenzoquinone formed by dissociation of the dimer is entirely

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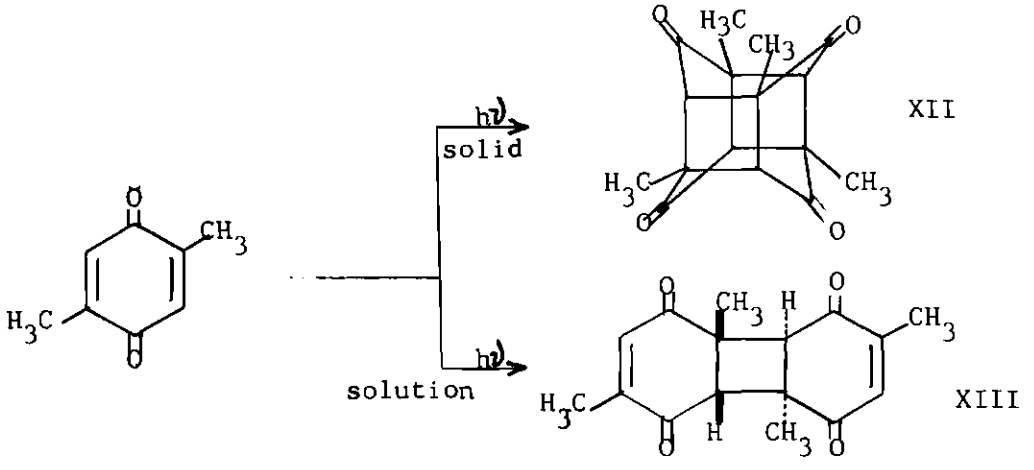
(8) E. Vogel and O. Roos, unpublished results (refer to E. Vogel, Angew Chem., 72, 4 (1960).

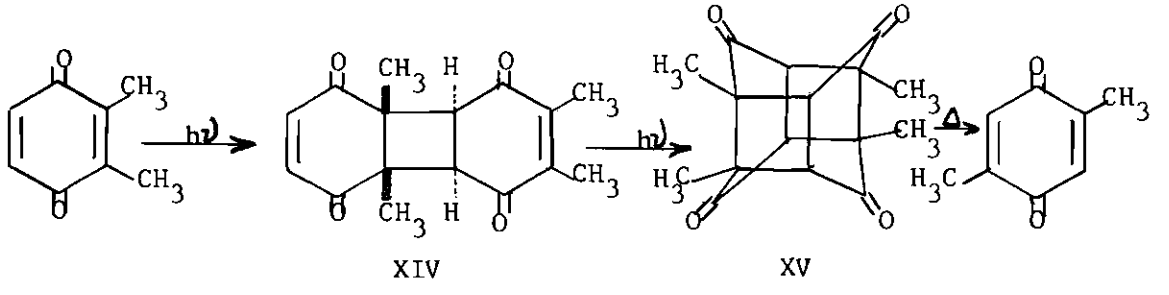
(9) P. Yates and M. J. Jorgenson, J. Am. Chem. Soc., 80, 6150 (1958).

(10) R. C. Cookson and J. Hudec, Proc. Chem. Soc., (London), 11 (1959).

the 2,5-isomer. Irradiation of a solution of dimethylbenzoquinone in ethyl acetate gives a light greenish-yellow dimer (XIII)(10) which decomposes to the monomer on heating. The yellow dimer (XIII) is not changed into the colorless one (XII) by further irradiation in the crystal or in solution, so that the two monomer units are probably joined trans.

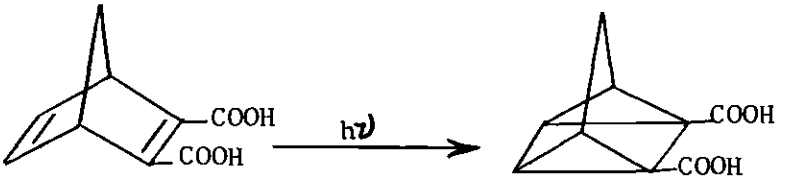


By short exposure to sunlight 2,3-dimethylbenzoquinone forms a pale yellow dimer (XIV)(11), which by further exposure to sunlight goes over to a colorless compound (XV). As (XIV) readily gives (XV) on further exposure to sunlight the six membered rings in (XIV) must be in cis position. Structure (XV) was assigned to the colorless dimer, since it gives among other compounds 2,5-dimethyl-p-benzoquinone on heating.



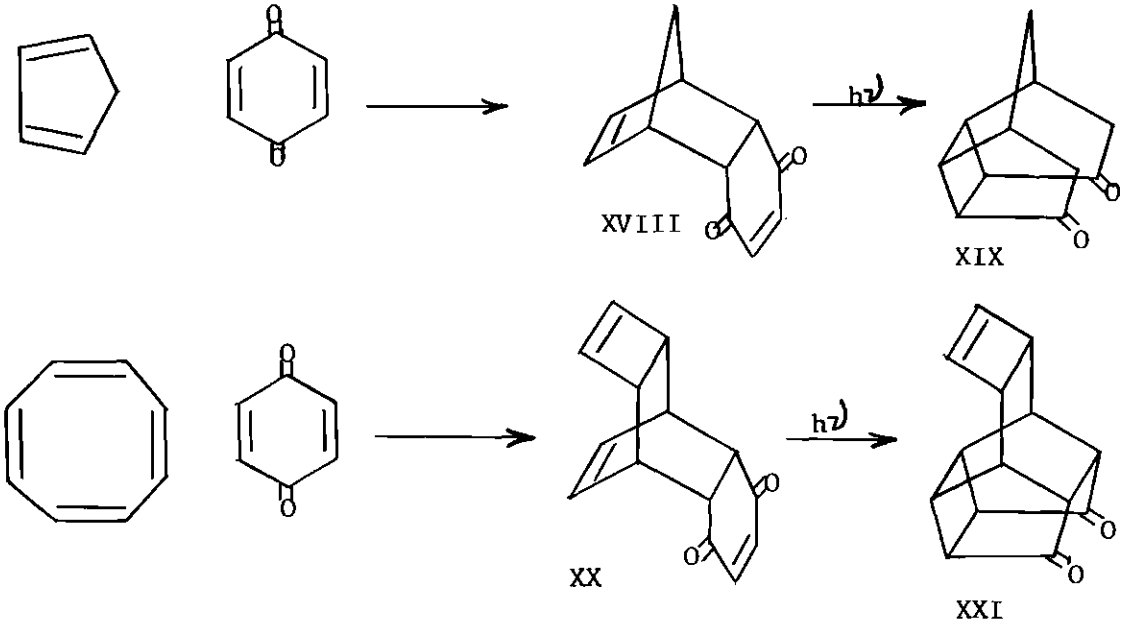
(11) W. Flaig, J. C. Salfeld, and A. Llanos, Angew. Chem., 72, 110 (1960).

An interesting example of photochemical isomerization is the irradiation of bicyclo[2,2,1]-heptadiene-2,3-dicarboxylic acid (XVI) to give its tetracyclic isomer (XVII)(12).



XVI XVII

Diels-Alder adducts (XVIII,XX) obtained from cyclopentadiene and cyclooctatetraene with p-benzoquinone have been converted by irradiation with a mercury-vapor arc into saturated isomers (XIX) and (XX) respectively with a cage structure(13).



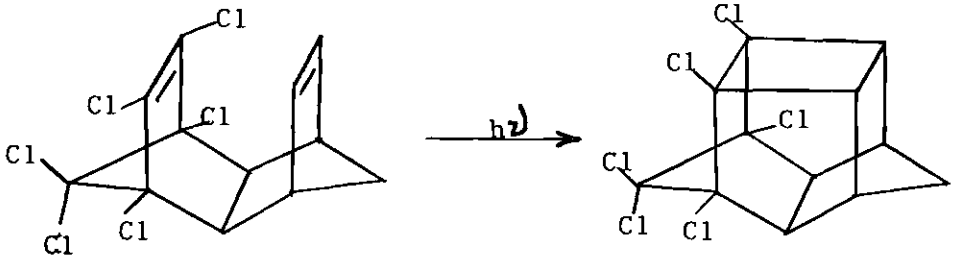
XVIII XIX

XX XXI

(12) S. J. Cristol and R. L. Snell, J. Am. Chem. Soc., 76, 5000 (1954).

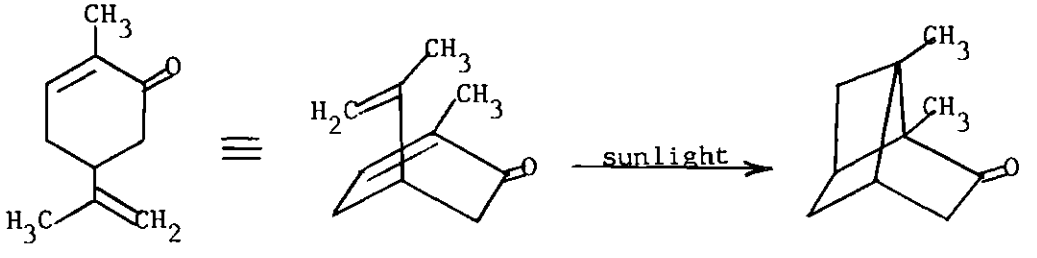
(13) R. C. Cookson and E. Crumwell, Chemistry and Industry (London), 1005 (1958).

Ultraviolet irradiation of the insecticide "isodrin" (XXII) yields a saturated isomer called "photodrin" (XXIII)(13). Of great theoretical interest is the closure of the four membered ring also on treatment of isodrin (XXII) with electrophilic reagents, in particular with acids or with bromine(13).



XXII XXIII

Another interesting case of photochemical isomerization is the conversion of carvone (XXIV) to carvonecamphor (XXV)(14).



XXIV XXV

Certain o-quinones and 1,2-diketones react in sunlight with olefins to form 1,4-dioxins(15). The reaction may be represented as follows:

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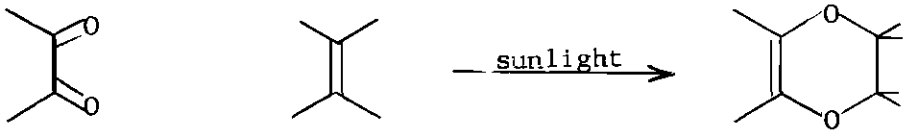
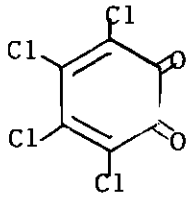
(14) G. Büchi and I. M. Goldman, J. Am. Chem. Soc., 79, 4741 (1957).

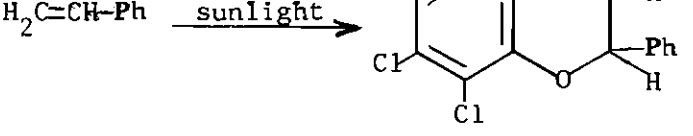
(15) See A. Schönberg and A. Mustafa, Chem. Revs. 40, 181 (1947) for a review.

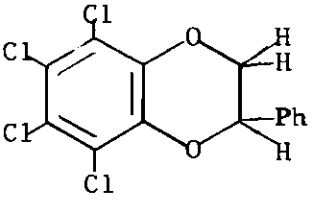


An interesting example of similar addition is the reaction of tetrachloro-o-benzoquinone (XXVI) with styrene in the presence of sunlight to give a compound of structure (XXVII)(16).



XXVI





XXVII

Many compounds having conjugated diene structure will undergo 1,4-addition with oxygen to yield cyclic peroxides when their dilute solutions are irradiated in the presence of sensitizers such as chlorophyll, eosin, or methylene blue(17). These reactions are of considerable theoretical and practical interest. An example is the photosyntheses of ascaridole(XXIX), which has been achieved by exposure to sunlight of a dilute solution of α-terpene(XXVIII) in the presence of

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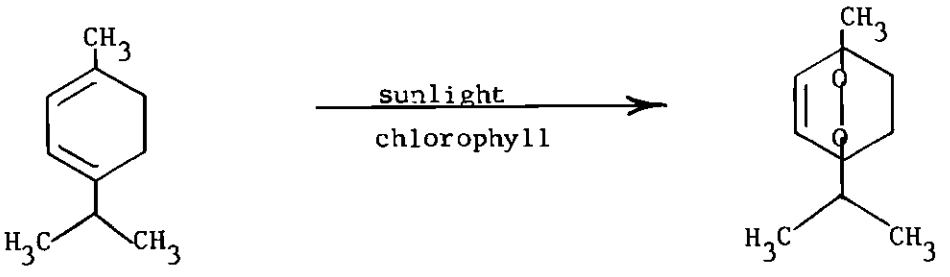
(16) A. Schönberg and N. Latif, J. Chem. Soc., 446 (1952).

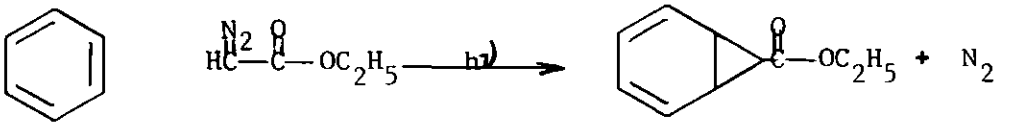
(17) See G. O. Schenck, Angew. Chem., 64, 12 (1952) for a review.

chlorophyll and molecular oxygen(18).



XXVIII XXIX

Norcaradienecarboxylic esters, prepared by the photolysis of diazoacetic ester in the presence of the corresponding aromatic hydrocarbon(19), have also been observed to yield transannular peroxides(17). This is illustrated for ethyl norcaradienecarboxylate (XXX).



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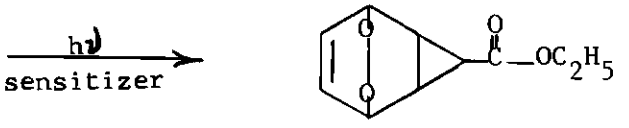

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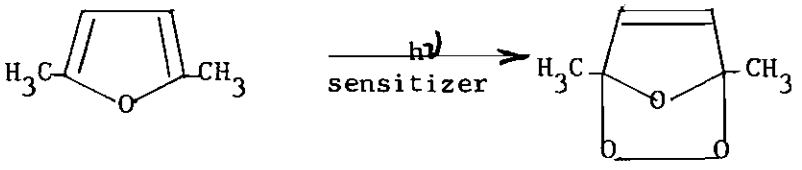
(18) G. O. Schenck and K. Ziegler, Naturwiss., 32,157 (1944).

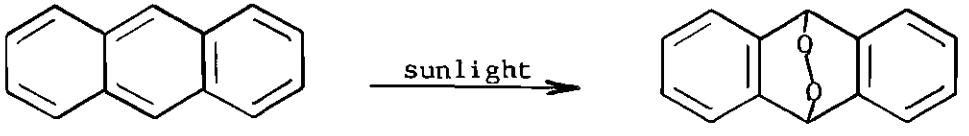
(19) K. B. Wiberg and T. W. Hutton, J. Am. Chem. Soc., 76, 5367 (1954).

An interesting special case of these reactions is observed with the furans, where oxygen adds in a 1,4-manner to give peroxides having an ozonoid type of structure. An example is the photosensitized oxidation of 2,5-dimethylfuran (XXXI)(17).



XXXI XXXII

Many polynuclear aromatic hydrocarbons also form transannular peroxides when their solutions are exposed to sunlight in the presence of air(20). Anthracene, for example, in carbon disulfide solution yields anthracene peroxide (XXXIII)(21).



XXXIII

Photolysis of cyclopentanone gives carbon monoxide and cyclobutane which on heating gives ethylene(22). Analogous to this reaction

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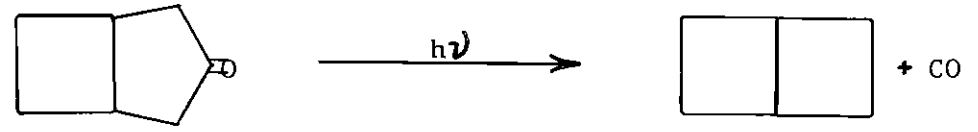
(20) See W. Bergman and M. J. McLean, Chem. Revs., 28, 367 (1941) for a review.

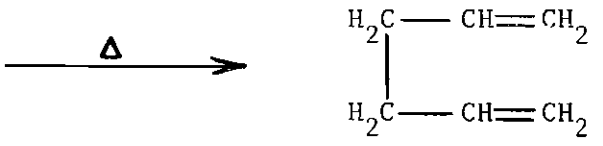
(21) C. Durfraisse and M. Gerard, Compt. rend., 201, 428 (1935).

(22) S. W. Benson and G. B. Kistiakowsky, J. Am. Chem. Soc., 64, 80 (1942).

is the photolysis of bicyclo[3,2,0]-heptanone-3(XXXIV) to give carbon monoxide and bicyclo[2,2,0]-hexane (XXXV) which on heating gives 1,5-hexadiene (XXXVI)(23).



XXXIV XXXV



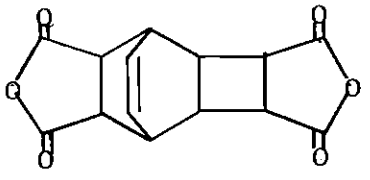
XXXVI

(23) S. Cremer and R. S. Srinivasan, Tetrahedron Letters, No. 21, 24 (1960).

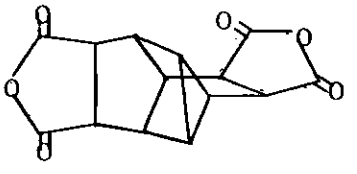
CHAPTER II

DISCUSSION OF PREVIOUS WORK ON THE PHOTOCHEMICAL ADDUCT OF BENZENE WITH MALEIC ANHYDRIDE

Irradiation of a solution of maleic anhydride in benzene with ultraviolet light gave a white crystalline product of m.p. 356-357° (dec.) in 13 per cent yield (based on maleic anhydride)(24). Angus and Bryce-Smith have reported in a recent communication(25) similar addition of maleic anhydride to benzene at 60° under the influence of ultraviolet light to give a product of m.p. 356° which they provisionally suggest has the structure (I). Taylor(24), on the other hand, suggested



I



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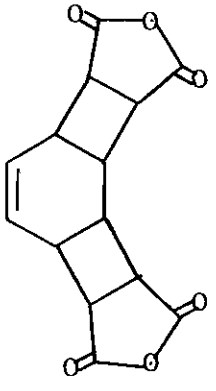
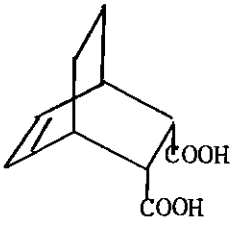


III



IV

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(24) J. W. Taylor, op. cit., pp. 43-45.

(25) H. J. F. Angus and D. Bryce-Smith, Proc. Chem. Soc. (London), 326 (1959).

structure (II) for this adduct.

The evidence upon which the inconclusive structural assignments are based is as follows. The adduct gave correct carbon-hydrogen analyses for $C_{14}H_{10}O_6$ and saponification equivalent of 68.4 as expected for an adduct from one mole of benzene combined with two moles of maleic anhydride(26). The adduct can be sublimed at 175° and 0.05 mm. pressure with slight decomposition. Molecular weight determinations by the melting-point depression techniques were unsuccessful in camphor, triphenylmethane, β-naphthol, biphenyl, or 2,4,6-tribromophenol apparently because the adduct is too insoluble in the melts from these compounds(26). The adduct gives upon refluxing with 0.2 N methanolic hydrogen chloride, a tetramethyl ester of m.p. 134.5-135.0°. The ester has correct carbon-hydrogen analysis and molecular weight (in camphor) for $C_{18}H_{22}O_8$(27).

The adduct on saponification gave a tetracarboxylic acid which after correction for ash had a satisfactory carbon-hydrogen analysis for $C_{14}H_{14}O_8$. The acid melts at 355-357° (dec.) with an initial decomposition at 125-200°, which evidently is loss of water. The acid upon hydrogenation(28) in glacial acetic acid over a 5 per cent platinum on carbon catalyst at room temperature and atmospheric pressure slowly absorbed over a 24 hour period one mole of hydrogen per mole of acid. The anhydride did not decolorize $KMnO_4$ in acetone and showed no reaction with

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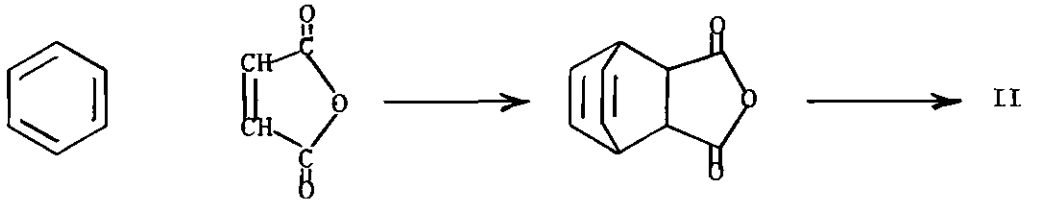
(26) J. W. Taylor, op. cit., pp. 46-47.

(27) Ibid., p. 49

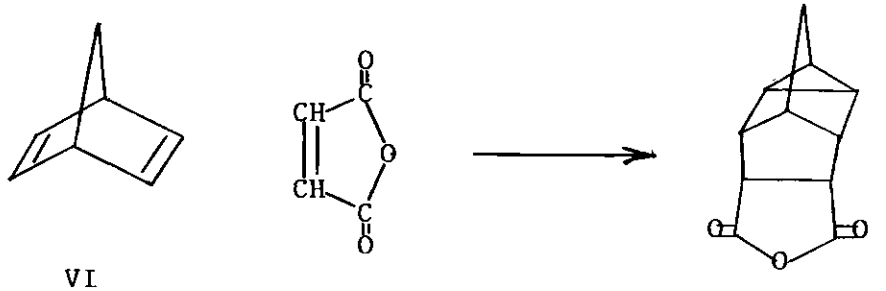
(28) Ibid., p. 48

bromine in boiling acetic acid under otherwise the usual conditions for these tests. Similarly, the methyl ester neither decolorized $KMnO_4$ in ethanol nor showed any reaction with bromine in methanol in the dark, the latter even after six days. On the basis of these tests for unsaturation the presence of a cyclopropane ring was postulated rather than a double bond(24). A simple structure for the adduct which contains a cyclopropane ring is structure II. This structure could be formed by 1,4-addition of one molecule of maleic anhydride to benzene to give V and then 1,5-addition of a second molecule of the anhydride to give II:



V

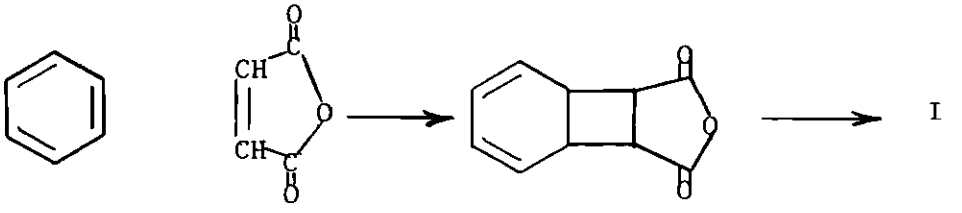
This 1,5-addition is analogous to the addition of maleic anhydride to bicyclo[2,2,1]hepta-2,5-diene (VI) under thermal conditions to give VII (29):



VI VII

(29) E. F. Ullman, Chem. and Ind. (London), 1173 (1958).

In agreement with a structure such as II, the sodium salt of the tetracarboxylic acid shows no ultraviolet absorption maxima(30) down to 210 mμ but does show "end-absorption" ($\epsilon_{220\ m\mu} \backsimeq 530$) much like that of the sodium salt of endo-cis-bicyclo[2,2,2]-5-octene-2,3-dicarboxylic acid (IV)(31)($\epsilon_{220\ m\mu} = 390$). Angus and Bryce-Smith(25) report for the tetracarboxylic acid a weak absorption maxima at 265 mμ ($\epsilon = 55$). These workers observed that per-acid titration of the tetramethyl ester inidcated the presence of one ethylenic bond per molecule and on the basis of this information and data rather similar to that given previously, suggested provisionally structure (I) for the adduct. They noted that structure (I) could reasonably be formed by 1,2-addition of one molecule of maleic anhydride to benzene to give VIII followed by 1,4-addition of a second molecule of the anhydride to give I:



VIII

If the second molecule of maleic anhydride adds to VIII by 1,2-addition rather than by 1,4-addition, then one would expect to obtain III rather than I. Furthermore, structures I, II, and III can exist in many

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(30) E. Grovenstein, Jr., private communication.

(31) K. Alder and G. Stein, Ann., 514, 15 (1934).

different forms. Many photochemical reactions are complex and do not follow the principle of minimum chemical change.

The nuclear magnetic resonance spectrum(32) of the tetramethyl ester of the benzene adduct in deuterochloroform shows the following proton chemical shifts(33), $\delta = 10^5$ (Hr-Hc)/Hr measured relative to water at the relative intensities given in parentheses (expressed as number of hydrogen atoms): + 0.16 (1.8): doublet at -0.13 (12.1); -0.195, -0.202, -0.24 (8.1). The first band is attributable to two ethylenic hydrogen atoms, though the absorption is nearer the value recorded(33) for tiglaldehyde or benzene than for cyclohexene. The band at -0.13 is in the region expected(33) for CH_3O and is of the correct intensity for four methoxyl groups; that this band is split into two bands of essentially equal intensity must mean that two of the methoxyl groups are in one type of environment (this cannot be ordinary spin-spin splitting because of the isolation of the hydrogen atoms of the carbomethoxyl groups from nearest neighboring hydrogen atoms by five or more intervening bonds). The last group of bands is not well resolved and appear near the region expected(34) for hydrogen on a carbon atom adjacent to a carboxyl or ethylenic group. It is significant that no absorption was found in the

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(32) J. W. Taylor, op. cit., pp. 38-39.

(33) L. H. Meyer, A. Saika, and H. S. Gutowsky, J. Am. Chem. Soc., 75, 4567 (1953).

(34) K. L. Rinehardt, Jr., W. A. Nilsson, and H. A. Whaley, ibid., 80, 503 (1958).

region expected for hydrogen on a cyclopropane ring (29,35). The infrared spectrum(36) of the adduct as the anhydride, the acid, or the methyl ester contains no absorption in the 6.73-6.92 μ region (frequency of CH_2 deformations)(37), while a band appears at 6.8 μ in the hydrogenated acid(38).

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(35) J. A. Pople, W. G. Schneider, and H. J. Bernstein, High-resolution Nuclear Magnetic Resonance, McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 236.

(36) J. W. Taylor, op. cit., p. 33.

(37) L. J. Bellamy, The Infra-red Spectra of Complex Molecules, 2nd. ed., Methuen and Co., Ltd., London, 1958, p. 13.

(38) J. W. Taylor, op. cit., p. 34.

CHAPTER III

DISCUSSION OF PRESENT WORK

Since the nuclear magnetic resonance absorption spectrum of the tetramethyl ester of the benzene adduct strongly indicates the presence of an olefin bond and the absence of a cyclopropane ring, the chemical evidence was examined in greater detail. While the sodium salt of the tetracarboxylic acid does not decolorize $KMnO_4$ in 5 minutes at room temperature, some decolorization occurs within a half hour. Similarly the tetracarboxylic acid in dilute hydrochloric acid solution slowly decolorizes bromine-water over a period of several hours. In sharp contrast, the sodium salt of the tetracarboxylic acid in aqueous solution reacts almost instantaneously with bromine to give, after acidification, a bromolactonic acid(39) which after reaction with excess diazomethane was isolated as a methyl ester (IX), m.p. 215-216°. This compound gave correct carbon-hydrogen analysis for $C_{17}H_{19}BrO_8$ and therefore appears to be a trimethyl ester of bromolactonic acid. This ester has infrared absorption at 5.63 and 5.80 μ near that expected(40) respectively for the carbonyl groups of a γ-lactone and of a carbomethoxyl group. Moreover, the sodium salt of the tetracarboxylic acid with aqueous iodine-potassium

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(39) E. Grovenstein, Jr., private communication.

(40) L. J. Bellamy, op. cit., p. 179.

iodide solution absorbs in 72 hours at room temperature 9.7 per cent or at 50° 70 per cent of one mole iodine per mole of acid. In comparative runs under similar conditions the sodium salt of endo-cis-bicyclo[2,2,2]-5-octene-2,3-dicarboxylic acid(IV)(31) immediately decolorizes aqueous $KMnO_4$ and absorbs 97 per cent of one molar equivalent of iodine in 23 seconds at room temperature (i.e., iodination occurs about a million times faster with the salt of IV than with the salt of the benzene-maleic anhydride adduct). In conclusion, the chemical evidence shows that the benzene-maleic anhydride adduct has one rather highly hindered double bond. Structure II for the adduct can therefore be discarded on the basis of both the chemical data and the nuclear magnetic resonance absorption spectrum.

The tetramethyl ester of the adduct when heated at reflux in methanol containing large excess of 98 per cent hydrazine gave 85 per cent yield of a product of m.p. 218-219° (dec.) which gave a fair analysis for $C_{16}H_{22}O_6N_4$ corresponding to a dihydrazide. The dihydrazide when distilled at 0.01 mm. lost hydrazine and gave cyclic hydrazide of m.p. 204.7-205.7° which gave good analysis for $C_{16}H_{18}O_6N_2$. The cyclic hydrazide when heated at reflux in methanol containing a large excess of hydrazine deposited crystals (87 per cent yield) of the starting dihydrazide. As judged by the behavior of the tetramethyl ester with hydrazine, two of the carbomethoxyl groups are considerably more readily attacked by hydrazine than the other two, and these reactive carbomethoxyl groups must be part of the same maleic acid radical since the dihydrazide may be pyrolyzed to a cyclic hydrazide. The chemical evidence, therefore, supports the nuclear magnetic resonance absorption data in indicating that two of the

carbomethoxyl groups of the tetramethyl ester are in an appreciably different environment than the other two carbomethoxyl groups. These data render structure III improbable in any of its likely stereochemical forms either because its double bond should be readily attacked by $KMnO_4$ or because it has two maleic anhydride radicals in equivalent positions. The most probable structure for the benzene-maleic adduct from these chemical reactions would be I.

In order to understand the reactions of the tetramethyl ester with hydrazine, derivatives of cis-cyclohexane-1,2-dicarboxylic acid anhydride were used as model compounds. When the corresponding dimethyl ester was heated at reflux with a large excess of 98 per cent hydrazine, a dihydrazide(41) of m.p. 229.5-230° (dec.) was obtained. The dihydrazide after pyrolysis gave the cyclic hydrazide (X) of m.p. 60-63° which gave analysis for $C_8H_{12}O_2N_2$. The cyclic hydrazide (X) on treatment with concentrated hydrochloric acid gave a product of m.p. 182-188.7° as expected for cis-cyclohexane-1,2-dicarboxylic acid(41a). Similar treatment of the starting dihydrazide gave a compound of m.p. 182-204°. This product gave negative tests for nitrogen and halogen and thus appears to be a mixture of cis- and trans-cyclohexane-1,2-dicarboxylic acids. Thus, under the conditions for the preparation of the dihydrazide, partial isomerization of the cis to the trans isomer occurred as might be expected from the work of Iashunskii(41).

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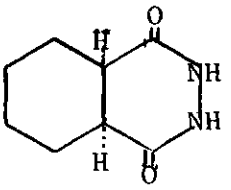
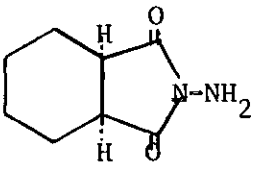
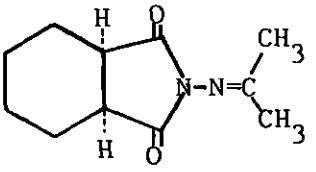
(41)(a) V. G. Iashunskii, J. Gen. Chem., U.S.S.R. (Eng. Trans.), 28, 1420 (1958); (b) H. Wieland, O. Schlichting, and W. v. Langdorff, Z. Physiol. Chem., Hoppe-Seyler's, 161, 78 (1926).



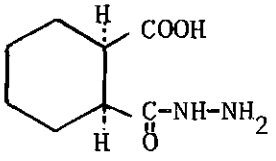
Xa



Xb



XI



XII

When the cyclic hydrazide (X) was dissolved in minimum amount of acetone and two volumes of n-hexane were added, there was isolated a crystalline substance of m.p. 124.0-125.5°. The product gave a satisfactory analysis for $C_{11}H_{16}O_2N_2$ which corresponds to an isopropylidene derivative of X. The only likely structure for the isopropylidene derivative appears to be XI. The ready formation of XI from X suggests that X has the structure Xb rather than the isomeric structure Xa. However, since Drew and Hatt(42) have shown that the more stable phthalhydrazide gives the same benzylidenederivative as the less stable N-aminophthalimide (though under more vigorous conditions), the reactions of X with acetone cannot be regarded as affording proof of structure Xb.

The potentiometric titrations of succinhydrazide as a monobasic acid has been cited(43) as evidence in favor of the hydrazide structure

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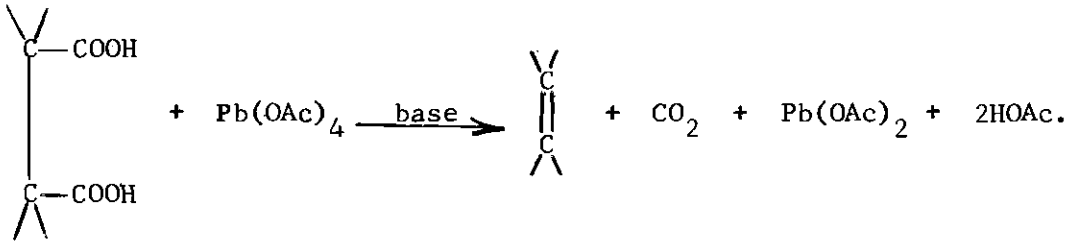
(42) H. D. K. Drew and H. H. Hatt, J. Chem. Soc., 16 (1937).

(43) H. Feur, G. B. Bachmann, and E. H. White, J. Am. Chem. Soc., 73, 4716 (1951).

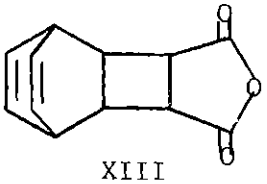
as opposed to the N-aminosuccinimide structure. When the cyclic hydrazide was dissolved in excess sodium hydroxide and back-titrated potentiometrically with hydrochloric acid, a neutralization equivalent of 172 (theory for monobasic acid $C_8H_{12}O_2N_2$, 168) was obtained. The direct titration with sodium hydroxide is difficult since X combines rather slowly with the base and the titrimetric data indicate that X undergoes hydrolysis to give the salt of XII under the conditions of the titration. Since either Xa or Xb might be expected to undergo ready hydrolysis to XII, the titration is also unable to distinguish between the two likely structures for X.

Much more conclusive evidence for the structure of the adduct has been provided by oxidation of a pyridine solution of the tetracarboxylic acid or better the anhydride itself with lead tetraacetate. Grob and co-workers(44) have reported that oxidation of several cis-1,2-dicarboxylic acids in presence of one to two molar equivalents of a base such as pyridine in benzene or acetonitrile as solvent gave 50-70 per cent yield of olefin in accord with the process:

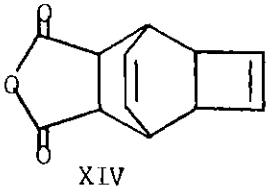


(44) C. A. Grob, M. Ohta, and A. Weiss, Angew. chem., 70, 343 (1948).

From oxidation of the benzene-maleic anhydride adduct with lead tetraacetate in pyridine at 50-62°, 56 per cent yield was obtained of a product of m.p. 167-168.7° which had satisfactory analyses for $C_{12}H_{10}O_3$. The same product, but in lower yield, was obtained by oxidation of the tetracarboxylic acid. During the lead tetraacetate oxidation, therefore, only one of the two maleic anhydride radicals of the adduct was oxidized. On the basis of structure (I) for the adduct, the lead tetraacetate oxidation could give either XIII or XIV for the product of composition $C_{12}H_{10}O_3$. Structure XIV can exist in four stereochemical forms (involving cis-fusion of the four- and five-membered rings to the [2,2,2]bicyclooctene system), one of these forms corresponds to the known(45) maleic anhydride adduct of cyclooctatetraene. It is remarkable, therefore, that the product $C_{12}H_{10}O_3$ from lead tetraacetate oxidation of the benzene-maleic anhydride adduct was found to be identical (mixed m.p. and infrared spectral comparisons) with the maleic anhydride adduct of cyclooctatetraene. This evidence conclusively establishes the structure of the benzene-maleic anhydride adduct as I in agreement with the brilliant provisional suggestions made by Angus and Bryce-Smith(25). There still remains obviously



XIII

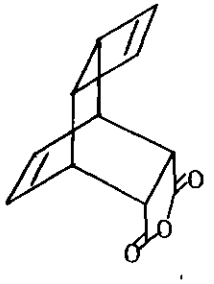


XIV

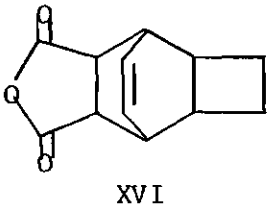
(45)(a) W. Reppe, O. Schlichting, A. Klager, and T. Toeppel, Ann., 560, 1 (1948); (b) A. C. Cope and C. G. Overberger, J. Am. Chem. Soc., 70, 1433 (1948).

unanswered the question of the stereochemical structure of the photochemical adduct.

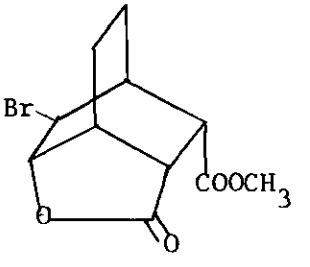
Structure I can exist in eight possible stereoisomeric forms with cis-fusion of the maleic anhydride groups. A key to the stereochemical form of the benzene-maleic anhydride adduct is found in the stereochemistry of the cyclooctatetraene-maleic anhydride adduct. Reppe(45)(a) and co-workers reported that this adduct gives a bromolactonic acid; therefore, the carboxyl groups of the adduct must be located in close proximity to one of the double bonds of the adduct. These workers have proposed that the cyclooctatetraene-maleic anhydride adduct has the stereochemical formula XV and, therefore, that bromolactone formations involves attack of bromine on the double bond in the six-membered ring to give a γ-lactone. Cope and co-workers(46) have proven that hydrogenation of the



XV



XVI



XVII

cyclooctatetraene-maleic anhydride adduct under mild conditions adds a mole of hydrogen to the double bond of the four-membered ring to give XVI rather than to the double bond of the six-membered ring as previously supposed(45)(a). Hence, Cope et al. have pointed out that bromolactone

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(46) A. C. Cope, A. C. Haven, Jr., F. L. Ramp, and E. R. Trumbull, ibid., 74, 4867 (1952).

formation may involve addition of bromine to the double bond of the four-membered ring; if this is the case, the bromolactone of XIV is a δ-lactone. In order to distinguish between these possibilities the infrared absorption spectrum of the bromolactonic ester of XIV was obtained and it showed carbonyl absorption at 5.69 and 5.76 μ. The first value agrees somewhat more closely with the absorption expected for a γ-lactone (5.62-5.68 μ) than for a δ-lactone (5.71-5.76 μ) while the second value corresponds to the value expected for the carbonyl group of an ester. In support of this interpretation the infrared spectrum of the bromolactonic ester of endo-cis-bicyclo[2,2,2]-5-octene-2,3-dicarboxylic acid (IV) was found to have a carbonyl absorption at 5.69 and 5.79 μ(47); therefore, γ-lactones in polycyclic structures may have carbonyl absorptions at 5.69 μ as found for the cyclooctatetraene adduct.

To obtain more conclusive proof of the stereochemistry of XIV, the reaction of the dihydro derivative XVI with bromine has been investigated. Of the four possible isomers of XIV with cis-orientation of the carbonyl groups, it may be seen that the carbonyl groups of the corresponding acid may be oriented near one of the other or none of the double bonds but cannot be oriented for a particular isomer such that bromolactone formation can take place with either double bond. Hence one method for determining which double bond is oriented near to the carboxyl groups is to remove one double bond by hydrogenation and see if the corresponding dihydro-derivative can form a bromolactone. Cope and coworkers reported(45) that dihydro-derivative XVI does not readily react

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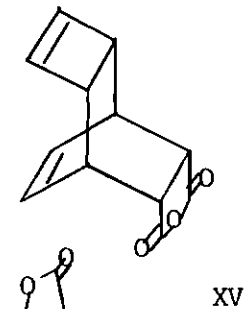
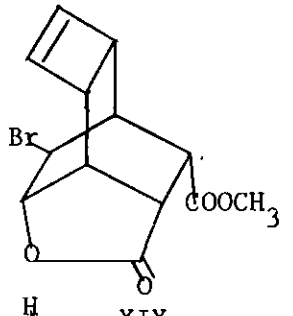
(47) E. Grovenstein, Jr., private communication.

with bromine but the experimental conditions tried were not mentioned. As in the case of benzene-maleic anhydride adduct, XVI did not decolorize a solution of bromine in carbon tetrachloride or acetic acid in 3 hours, on the other hand the potassium salt of XVI in water reacted almost instantaneously with one molar equivalent of bromine to give a good yield of crystalline product of m.p. 243~244° (dec.) which had the expected composition for a bromolactonic acid $C_{12}H_{13}O_4Br$. The corresponding crystalline monomethyl ester, $C_{13}H_{15}O_4Br$, had carbonyl absorption at 5.65 and 5.77 μ as expected for the methyl ester of γ-lactone. Hence the carbonyl groups of XVI are oriented near to the double bond in the six-membered ring rather than near the double bond of the four-membered ring. Thus structure XV of Reppe et al.(45)(a) is correct in so far as this particular structural evidence is concerned.

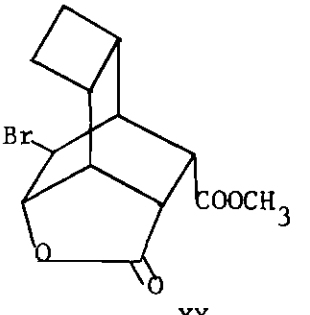
There was never, however, any compelling evidence for the steric orientation of the four-membered ring of XV relative to the cyclohexene ring. Structure XVIII would appear to be equally probable and has been



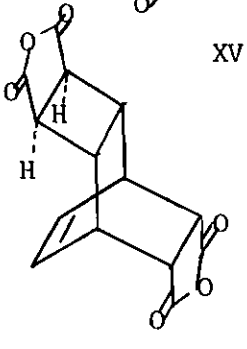
XVIII



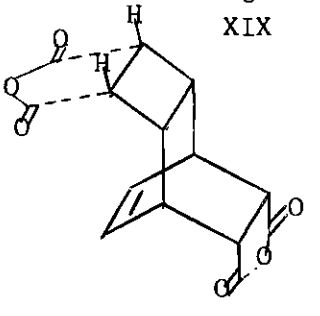
XIX



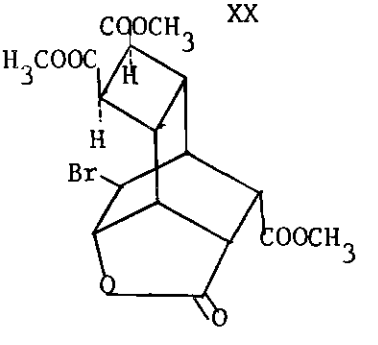
XX



XXI



XXII



IX

written by Abel, Bennett, and Wilkinson(48). These workers found that the cyclooctatetraene-maleic anhydride adduct forms a crystalline rhodium-(I) chloride complex which is believed to involve chelation by the diolefin group to one rhodium atom. The two double bonds in the cyclooctatetraene-maleic anhydride adduct are, therefore, almost certainly oriented as in XVIII especially since bicyclo[2,2,1]-heptadiene (norbornadiene) forms a similar rhodium(I) chloride complex(48).

If no changes in steric orientation of groups occur during the oxidation of the benzene-maleic anhydride adduct (I) by lead tetraacetate to give XVIII, then only structures XXI and XXII need be considered for the photochemical adduct. No changes in stereochemistry are expected to occur during the lead tetraacetate oxidation because of the mild conditions of the reaction and the speed of the oxidative decarboxylation. These expectations appear to be confirmed since the tetracarboxylic acid of I gave XVIII as the only insoluble acidic product while at least some of the trans-acid(45)(a) would have been expected if any isomerization had occurred at the centers bearing the carboxyl groups. Furthermore, the photochemical adduct I gave a bromo-γ-lactone(39) and hence one acid anhydride group in I must be oriented as in XVII. Of the two structures XXI and XXII, structure XXI appears much more probable than XXII. The location of anhydride group A as in XXI rather than as in XXII is implied from the observations: (1) hydrazine readily attacks only two adjacent carbomethoxyl groups of the corresponding tetramethyl

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(48) E. W. Abel, M. A. Bennett, and G. Wilkinson, J. Chem. Soc., 3178 (1959).

ester, (2) lead tetraacetate oxidation removes the two carbonyl groups of anhydride A and hence these are implicated as the less hindered carbonyl groups, (3) the alternative location of the carbonyl groups in A as in XXII would place these groups very close to the double bond and models indicate that the carbonyl groups in A would then be more hindered than the carbonyl groups in B, (4) bromolactone formation gives a γ-lactone as expected from XXI while a δ-lactone might be expected from XXII.

In conclusion structure XXI is assigned as the probable stereochemical structure of the photochemical adduct with maleic anhydride. This structure contains a double bond which is hindered on either side from the approach of external reagents. Structure XXI, therefore, accounts for the remarkable unreactivity of the double bond toward permangante and halogens.

CHAPTER IV

PHOTOCHEMICAL ADDUCTS OF TOLUENE AND p-XYLENE WITH MALEIC ANHYDRIDE

Ultraviolet irradiation of a solution of maleic anhydride in toluene gave a pale yellow liquid product. Schenck and Steinmetz in a recent communication(49) reported a 1:2 adduct between toluene and maleic anhydride by photochemical method using a photosensitizer such as benzophenone. The product they reported had a wide melting point range of 250-270° (dec.)since it is a mixture of several isomers. After esterification they were able to isolate two methyl esters of melting points 105-107° and 163-165°. These workers in their brief report make no mention of a 1:1 adduct.

Hydrolysis of the liquid product obtained in the present work gave, in part, an acid of m.p. 162-163° which had a satisfactory C,H-analysis for $C_{11}H_{12}O_4$ and therefore appears to consist of one mole of toluene combined with one mole of maleic anhydride(50). The remainder of the product from this reaction was an oil which was esterfied. The resulting methyl ester could be distilled at 0.015 mm. at a bath temperature of 145° to give a pale yellow oil which had a fair C,H-analysis for $C_{13}H_{16}O_4$ and therefore appears to consist of one mole of toluene combined with one mole of dimethyl maleate. Gas chromatography of the methyl ester at 247 or 288° using a Fisher-Gulf Partionmeter Model 300 provided

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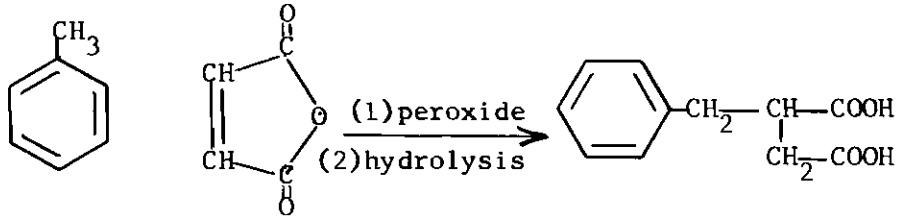
(49) G. O. Schenck and R. Steinmetz, Tetrahedron Letters, No. 21, p. 6 (1960).

(50) E. Grovenstein, Jr., private communication.

with a fine-brick packing impregnated with silicone oil, gave two strong, two medium, and four rather weak bands(50). Evidently the methyl ester consists of a complex mixture of compounds although at the temperature of the chromatogram some thermal isomerization may be taking place.

The ester prepared from the liquid acid from another run with toluene and maleic anhydride was distilled at 0.15 mm. and at a temperature up to 165°, however the ester which distilled amounted to only 20 per cent by weight of the starting acid. This volatile ester upon vapor phase chrmatography gave only a single peak. This ester on saponification gave an acid of m.p. 158-160°.

The peroxide catalyzed addition of toluene to maleic anhydride has been reported(51) to give benzylsuccinic of m.p. 161-162° and it has been mentioned that such reactions are also catalyzed by ultraviolet light



but no details of the light catalyzed reaction are given. This report along with the data reported here definitely indicates that the crystalline acid obtained from the liquid adduct in the present work is benzylsuccinic acid. The free-radical nature of this reaction has also been verified by the addition of the inhibitor hydroquinone which decreased

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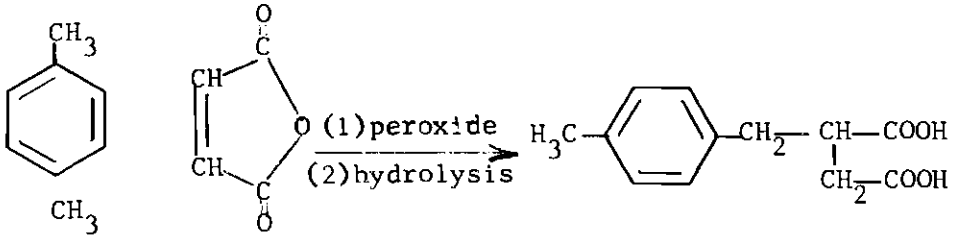
(51) W. G. Bickford, G. S. Fischer, F. G. Dollear, and C. E. Swift, J. Am. Oil Chemists' Soc., 25, 251 (1948).

the yield of the liquid product.

Irradiation of a solution of maleic anhydride in p-xylene gave a syrupy liquid product. From this there was obtained in part a crystalline substance of m.p. 86-87° which gave a satisfactory C,H-analysis for $C_{12}H_{12}O_3$ as expected for an adduct of one mole of p-xylene combined with one mole of maleic anhydride. On saponification the crystalline anhydride gave an acid of m.p. 115-117°. The liquid fraction on esterification and distillation at 0.05 mm. and bath temperature of 160° gave a pale yellow liquid. This ester on saponification gave a crystalline material of m.p. 115-117°.

Peroxide catalyzed addition of p-xylene to maleic anhydride has also been reported(51,52) to give p-methylbenzylsuccinic acid of m.p. 114-115°, which indicates strongly that the crystalline acid obtained from the liquid adduct is p-methylbenzylsuccinic acid.



(52) H. Shechter and H. C. Barker, J. Org. Chem., 21, 1473 (1956).

CHAPTER V

EXPERIMENTAL DETAILS

Purification of Starting Materials

Benzene.--Benzene used in the irradiation experiments was a thiophene-free grade (Matheson, Coleman, and Bell). However, to make sure that no thiophene was present, it was shaken several times with concentrated sulfuric acid until there was no color in the sulfuric acid layer. The product was washed with water twice and then with dilute sodium bicarbonate once. It was washed with water again and then dried over anhydrous calcium chloride. The benzene was finally distilled and dried over sodium wire.

Toluene.--Thiophene free toluene was used in the irradiation experiments. Thiophene was removed by the same procedure described for benzene.

p-Xylene.--Eastman's White Label grade was used after removing traces of thiophene by the same procedure described for benzene.

Maleic Anhydride.--Freshly distilled maleic anhydride was used in all the irradiation experiments.

Acetone.--Commercial acetone was distilled over potassium permanganate before using as a solvent. About 20 g. of potassium permanganate was used for distilling 2 l. of acetone.

Preparations

Benzene and Maleic Anhydride Adduct.--Freshly distilled maleic anhydride (118 g., 1.2 moles) was dissolved in 100 ml. of acetone, and to this solution was added 120 ml. of benzene. This solution was then

irradiated for 25 hours with a 1000-watt Hanovia mercury-arc lamp in a water-cooled quartz cell. The white crystals which precipitated on the walls of the cell were filtered by suction and washed with acetone to remove any maleic anhydride. The weight of the product thus obtained was 10.5 g. Another 6.5 g. of adduct was recovered from the solution after evaporating the solvent and then treating the residue with 200 ml. of boiling acetone on a steam bath in order to dissolve the unreacted maleic anhydride. The total yield was 17.0 g. or 10.3 per cent based on maleic anhydride and a molecular weight of 274 for the adduct anhydride. Prolonged irradiation beyond 25 hours did not improve the yields and gave a more colored product and solution.

A small portion of adduct was refluxed with acetic anhydride for one-half hour, filtered off, and then dried. It was vacuum sublimed slowly at 0.015 mm. and a bath temperature of 240-250° to give a product of m.p. 355-357° (dec.).

Tetracarboxylic Acid of Benzene-Maleic Anhydride Adduct.--The adduct (25.5 g.) was refluxed with 154 ml. of 2.417 N potassium hydroxide (4 equivalents and 100 ml. of water for 5 hours. The solution was cooled, then filtered to remove suspended impurities, and acidified with hydrochloric acid. A white crystalline solid precipitated. The crystals were filtered off and dissolved in hot water. The solution upon cooling deposited 20.0 g. of white crystals. A small portion was crystallized 4 times from hot water to give a product of m.p. 356-357° (dec.)

Anal. Calcd. for $C_{14}H_{14}O_8$: C, 54.20; H, 4.55; Found: C, 54.46, 54.69; H, 4.16, 4.21[1]

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[1]All analyses were done by Galbraith Microchemical Laboratory, Knoxville, Tennessee.

Tetramethyl Ester of Benzene-Maleic Anhydride Adduct.--The adduct (20.0 g.) was refluxed with 300 ml. of anhydrous methanol which was 0.2 N in dry hydrogen chloride. The solution was concentrated to 50 ml. on a steam bath and on cooling gave 20.0 g. of white crystalline precipitate. A small portion was recrystallized from methanol twice to give a product of m.p. 134.5-135.0°.

Tetramethyl Ester of Tetracarboxylic Acid of Benzene-Maleic Anhydride Adduct.--Tetracarboxylic acid (15.0 g.) was esterfied with 200 ml. of anhydrous methanol which was 0.2 N in anhydrous hydrogen chloride using the same procedure as in the case of anhydride. There resulted 14.5 g. of ester. A small portion was recrystallized from methanol twice to give a product of m.p. 133.0-133.4°. A mixed melting point with the ester from the anhydride showed no depression. The infrared spectrum was also identical with the ester obtained from the anhydride and therefore the two esters appear to be identical.

Dihydrazide of Benzene-Maleic Anhydride Adduct.--The methyl ester of the benzene-maleic anhydride adduct (2.00 g.) was heated at reflux with 5.0 ml. of 98 per cent hydrazine in 25 ml. of methanol for 2 hours. A white crystalline solid precipitated during the reaction and after separation by filtration from the cold reaction mixture, amounted to 1.70 g. (85 per cent yield). The melting point was variable with the rate of heating. It melted at 231.0-233.0° (dec.) when the rate of heating was 4°/min, and at 218-219° (dec.) when the rate of heating was 1°/min. It could not be recrystallized from common organic solvents such as ether, benzene, n-hexane, methanol, ethanol and dioxane.

Pyrolysis of Dihydrazide.--Since the dihydrazide could not be recrystallized from common organic solvents, purification by sublimation was attempted. The dihydrazide (1.3 g.) was vacuum sublimed at 0.01 mm. and a bath temperature of 270°. In 30 minutes the sublimation was complete, and 1.0 g. of product was obtained. Unlike the starting dihydrazide, it was soluble in methanol. A small portion was recrystallized twice from methanol to give a white crystalline product of m.p. 202.7-203.7°.

Anal. Calcd. for $C_{16}H_{18}O_6N_2$: C, 57.48; H, 5.436; N, 8.38; Found: C, 56.71, 56.75; H, 5.26, 5.62; N, 8.59, 8.99.

Since there is an appreciable difference of C, H, and N values obtained from microchemical analysis and the calculated values based on $C_{16}H_{18}O_6N_2$, it was further purified by vacuum sublimation (240° and 0.01 mm.), and one recrystallization from methanol to give a compound of m.p. 204.7-205.7°.

Anal. Calcd. for $C_{16}H_{18}O_6N_2$: C, 57.48; H, 5.436; N, 8.38; Found: C, 57.65; H, 5.55; N, 8.32.

Treatment of Cyclic Hydrazide with Hydrazine.--The cyclic hydrazide (0.5 g.) obtained above by pyrolysis of the dihydrazide was heated at reflux with 2.0 ml. of 98 per cent hydrazine in 25 ml. of methanol for 2 hours. The white crystalline solid which precipitated during the reaction was filtered off, washed with methanol, and dried to give 0.48 g. of product. Just as in the case of the dihydrazide obtained from tetramethyl ester the melting point was variable depending upon the rate of heating. It melted at 229.2-231° (dec.) when the rate of heating was

4°/min, and at 219.2-219.8° (dec.) when the rate of heating was 1°/min. Since this compound has a similar melting point to that of the dihydrazide from the tetramethyl ester, they were mixed in equal amounts and a mixed melting point was determined. Heated in the vicinity of the melting point at 1°/min., the mixture melted at 219.0-219.8° (dec.). The infrared spectra of both compounds were also identical. These data indicate that the two dihydrazides are identical.

Since the dihydrazide obtained from the cyclic hydrazide was purer than the one obtained from the tetramethylester, the former was sent for micro chemical analysis.

Anal. Calcd. for $C_{16}H_{22}O_6N_4$: C, 52.45; H, 6.05; N, 15.29; Found: C, 51.8; H, 6.01; N, 15.36.

Treatment of Tetramethyl Ester with Hydrazine under Vigorous Conditions.--The ester (2.0 g.) was heated at reflux with 5.0 ml. of 98 per cent hydrazine for 15 minutes. To this was added 20 ml. of methanol and heating at reflux was continued for 3 hours. A dull white solid precipitated from the solution, and this was filtered off and dried to give 1.6 g. of product. When this compound was boiled with 10 ml. of dry methanol for 30 minutes and filtered a white product was obtained of m.p. 211.0-213.0° (dec.). This compound was insoluble in ether, benzene, n-hexane, methanol, ethanol, and dioxane. It could not be vacuum sublimed at 0.015 mm. and a bath temperature of 300°.

Anal. Calcd. for $C_{14}H_{22}O_4N_8$: N, 30.59: Found: N, 28.30

Dimethyl Ester of cis-Hexahydrophthalic Acid.--Hexahydrophthlic anhydride (70.0 g.) was heated at reflux with 350 ml. of methanol saturated with dry hydrogen chloride for 2 hours. After removing the solvent

by evaporation there resulted an oil which was dissolved in ether, washed with a dilute solution of sodium bicarbonate several times, and finally washed with water. The ether solution was then dried over anhydrous magnesium sulfate overnight and on evaporating the ether a colorless liquid with a pleasant odor was obtained. The product was distilled *in vacuo* to give 65 ml. of colorless liquid of b.p. 132-133° (13 mm.).

Dihydrazide of Cyclohexane-1,2-dicarboxylic Acid.--Dimethyl *cis*-cyclohexane-1,2-dicarboxylate (40.0 g.) was heated at reflux with 40.0 ml. of 98 per cent hydrazine for 15 minutes. Just enough methanol was added to give a homogeneous solution and the mixture was heated at reflux for one hour. Concentration of the solution gave a crystalline product which was washed with 25 ml. of methanol and dried to give 38.0 g. of dihydrazide. A small amount was crystallized twice from 85 per cent aqueous methanol to give a white crystalline solid. The compound melted at 243.0-245.0° (dec.) when the rate of heating was 4°/min., and at 229.5-230.4° (dec.) when the rate of heating was 1/2°/min. (recorded: *trans*-dihydrazide[1] 229-231°; *cis*-dihydrazide[1] 123.0-124.5° and then 228.5-229.5°; unspecified isomer[2] 245°).

Pyrolysis of Dihydrazide of Cyclohexane-1,2-dicarboxylic Acid.--The dihydrazide (45 g.) was pyrolyzed at a bath temperature of 280-290° and a pressure of 20 mm. to give a distillate of b.p. 220-230°. The distillate (30 g.) solidified on cooling and had a m.p. 55-60°. A second distillation gave 28.0 g. of a colorless product of b.p. 152-160° at 0.5 mm. and of m.p. 60-63°. Redistillation through a short fractionating column gave

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[1] See reference (41)(a).

[2] See reference (41)(b).

20.0 g. of cyclic hydrazide of m.p. 60.4-62.9°.

Anal. Calcd. for $C_8H_{12}O_2N_2$: C, 57.13; H, 7.19; N, 16.66 Found: C, 57.42; H, 7.02; N, 16.42.

Hydrolysis of Dihydrazide and Cyclic Hydrazide.--The dihydrazide of cyclohexane-1,2-dicarboxylic acid (3.0 g.) with 30 ml. of concentrated hydrochloric acid at reflux for 30 minutes gave 1.3 g. of product of m.p. 182-204°. This product upon sodium fusion gave a negative test for nitrogen and halogen and thus appears to be a mixture of cis and trans cyclohexane-1,2-dicarboxylic acids. Similar treatment of the cyclic hydrazide (3.0 g.) with 30 ml. concentrated hydrochloric acid gave a product (2.6 g.) of m.p. 187.3-188.7° as expected for cis-cyclohexane-1,2-dicarboxylic acid (recorded[1], m.p. 189.5-190.5°).

Isopropylidene Derivative of Cyclic Hydrazide of cis-Cyclohexane-1,2-dicarboxylic Acid.--The cyclic hydrazide was dissolved in a minimum amount of acetone and two volumes of n-hexane were added. The mixture was heated on a steam bath and the supernatent hexane layer was separated. Two similar hexane extractions were made and from the combined hexane extracts crystals in the form of needles were obtained on cooling. These after another similar crystallization from acetone-n-hexane had a m.p. of 124.0-125.5° (with previous sintering at 120°).

Anal. Calcd. for $C_{11}H_{16}O_2N_2$; C, 63.44; H, 7.74; N, 13.45; Found: C, 63.89; H, 7.98; N, 13.12.

Iodometric Titrations of Benzene-Maleic Anhydride Adduct.--An accurately weighed amount of adduct was saponified with a slight excess of sodium

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[1] See reference (41)(a)

hydroxide solution for one hour. It was then neutralized with dilute hydrochloric acid using phenolphthalein as indicator. After neutralization it was made to a known volume in a volumeric flask . Three 20 ml. portions of the above solution were withdrawn into three glass stoppered Erlenmeyer flasks. To each of these were added 20 ml. of iodine solution. After the reaction time specified the solutions were acidified and titrated with a standard solution of sodium thiosulfate using starch as an indicator. The following results were obtained in three series of experiments (0.018 M in the salt of acid, 0.025 M in I_2, and 0.0137 M NaI):

Time (hrs.)	Temperature (°C)	Reaction (%)
4	25	no appreciable reaction
72	25	9.73
72	50	70.5

Iodometric Titrations of 1,3-Cyclohexadiene-Maleic Anhydride Adduct.--A procedure similar to that used in the case of the benzene-maleic anhydride adduct was employed. Instead of acetic acid, hydrochloric acid was used to acidify the solution before titrating for unreacted iodine. Reaction in this case was very fast - in about 23.5 sec. at 25° 97.5 per cent of the iodine was consumed.

Oxidation of cis-Cyclohexane-1,2-dicarboxylic Acid with Lead Tetraacetate.--cis-Cyclohexane-1,2-dicarboxylic acid (6.0 g.) was dissolved in 30 ml. of benzene and 5 ml. of pyridine (2 equivalents) was added. To this solution at 60° was added lead tetraacetate (15.0 g., 2 equivalents). A vigorous evolution of carbon dioxide took place for about 5 minutes. Heating at 60° was continued for one hour; after this time the solution

was distilled to separate benzene and any cyclohexene that was obtained from the oxidation. In order to detect the presence of cyclohexene in the distillate an infrared spectrum of an authentic 1:6 mixture of cyclohexene and benzene was compared with that of this distillate. The two spectra showed identical location of all bands. Oxidation, therefore, had taken place to give cyclohexene.

Oxidation of Benzene-Maleic Anhydride Adduct with Lead Tetraacetate.--The anhydride of the adduct (5.0 g., 0.018 mole) was dissolved in 200 ml. of hot pyridine (which had been dried over KOH pellets and freshly distilled). Lead tetraacetate (9.0 g., 0.020 mole) was added and the pyridine solution was maintained at 70-80° for one hour. During the first five minutes of reaction there was a vigorous evolution of carbon dioxide. The solvent was removed in vacuo with aid of a steam bath. The dark brown residue was acidified with hydrochloric acid and extracted with ether three times. The etheral extracts were combined, washed with water twice, and dried over anhydrous magnesium sulfate. After removal of the ether, 1.5 g. of crystalline product was obtained. This was sublimed at 0.025 mm. at a bath temperature of 170° to give 1.45 g. (39.5 per cent yield) of crystalline sublimate. After two crystallizations from chlorobenzene the product had a m.p. of 166.9-168.7°.

Anal. Calcd. for $C_{12}H_{10}O_3$: C, 71.28; H, 4.98; Found: C, 70.89, 70.92; H, 4.80, 4.95.

A sample of the maleic anhydride addition product of cyclooctatetraene was prepared[1] by heating maleic anhydride (5.0 g.) with

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[1] See reference (45).

cyclooctatetraene (5.2 g.) under a nitrogen atmosphere at a bath temperature of 180° for 30 minutes. After this time the reaction mixture when cooled gave a crystalline product. This product was filtered off and washed with ether to give 9.11 g. of product. A small portion of this product after sublimation in vacuo and recrystallization from chlorobenzene had a m.p. 167.3-168.7° and gave no depression of m.p. when mixed with the product from the lead tetraacetate oxidation. The two products had identical infrared spectra.

A higher yield was obtained from reaction of 2.40 g. (0.00875 mole) of the anhydride of the adduct with 5.80 g. (0.013 mole) of lead tetraacetate in 85 ml. of pyridine maintained at 50-62° for one hour. The reaction mixture after standing over night was worked up as previously. After one sublimation in vacuo the product amounted to 1.00 g. (56 per cent yield) of material of m.p. 166.6-168.3°. A similar oxidation with lead tetraacetate in which 2 moles of lead tetraacetate were used per mole of anhydride gave only 34 per cent yield.

Oxidation of the tetracarboxylic acid of the adduct was hindered, at least in part, by the low solubility of the acid in pyridine. Tetracarboxylic acid (5.0 g., 0.16 mole) did not dissolve completely in 150 ml. of boiling pyridine. To the mixture at 95-100° was added 10.0 g. (0.023 mole) of lead tetraacetate and the whole kept at this temperature for one hour. The reaction product was worked up as with anhydride. From the ether extracts 0.50 g. of crude product was obtained. After one recrystallization from methanol the product amounted to 0.35 g. of material of m.p. 160-161.5°. Another recrystallization from methanol gave a product of m.p. 167.1-167.9°. It gave no depression of m.p. (167.3-

167.8°) when mixed with the maleic anhydride adduct of cyclooctatetraene. The two products had identical infrared spectra.

Hydrogenation of Cyclooctatetraene-Maleic Anhydride Adduct[1].--The anhydride (2.00 g. , 9.9 mole) was dissolved in a solution of 2.0 g. of potassium hydroxide in 50 ml. of water. The catalyst (5 per cent palladium on carbon, 2.0 g.) was suspended in 25 ml. of water and reduced with hydrogen. It absorbed about 40 ml. of hydrogen. The alkaline solution of the compound was introduced into the hydrogenation flask and hydrogenation was continued while stirring the solution with a magnetic stirrer. When the volume of hydrogen absorbed reached 254 ml., the hydrogenation was stopped and the alkaline solution was then filtered free from catalyst and acidified with 50 per cent hydrochloric acid. The white fluffy precipitate thus obtained was filtered off and dried. The product was sublimed at 0.02 mm. at a bath temperature of 170° to give 1.75 g. of crystalline compound. It had a m.p. of 141-142.5°. (Recorded[1] m.p. 144-145°).

Bromolactonic Acid of Cyclooctatetraene-Maleic Anhydride Adduct.--The anhydride (2.00 g., 9.9 mole) was dissolved in a solution of 2.0 g. of potassium hydroxide in 50 ml. of water. The excess of alkali was neutralized with dilute hydrochloric acid using phenolphthalein as indicator. To this neutral solution was added in 0.10 ml. portions 0.50 ml. of liquid bromine, and then a slight excess was added (0.10 ml.) to obtain a permanent pale yellow color. Then the solution was acidified with 10 per cent hydrochloric acid and the resulting precipitate was filtered off and dried to

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[1] See reference (45)(b).

give 2.71 g. of crude product. This was crystallized from 95 per cent ethanol to give 2.5 g. of product of m.p. 241.8-243.3° (dec.) (Recorded[1] m.p. 238° (dec.).)

Bromolactonic Ester of Cyclooctatetraene-Maleic Anhydride Adduct.--The bromolactonic acid of the adduct (1.5 g.) was dissolved in tetrahydrofuran, and a solution of diazomethane in ether was added until a pale yellow color persisted. The solvents were then removed by evaporation and 1.5 g. of crystalline product was obtained. After two recrystallizations from methanol the product had a m.p. of 178.6-179.6° (Recorded[1] m.p. 177-178°). The infrared spectrum showed carbonyl bands at 5.688 μ and 5.758 μ which are characteristic, respectively, of γ-lactones and normal saturated esters.

Bromolactonic Acid of Hydrogenated Cyclooctatetraene-Maleic Anhydride Adduct.--The dihydro derivative of the maleic anhydride adduct of cyclooctatetraene (2.00 g. 9.8 mole) was dissolved in a warm solution of 3.0 g. of potassium hydroxide in 50 ml. of water and the solution was filtered to remove traces of suspended material. The solution was neutralized to a phenolphthalein end-point with dilute hydrochloric acid then bromine was added dropwise with shaking. The color of bromine disappeared rapidly during addition of 0.45 ml. (8.8 mmole) but a permanent yellow color remained after addition of 0.05 ml. (1.0 mmole) more bromine. Acidification gave a precipitate which after separation by filtration and recrystallization from 95 per cent ethanol amounted to 2.50 g. (85 per cent yield) of bromolactonic acid of m.p. 243.3-243.8° (dec.).

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[1]See reference (45)(a).

Anal. Calcd. for $C_{12}H_{13}O_4Br$: C, 47.86; H, 4.35; Br, 26.54; Found: C, 47.73, 47.81; H, 4.52, 4.40; Br, 26.61.

Bromolactonic Ester of Hydrogenated Cyclooctatetraene-Maleic Anhydride Adduct.--The bromoloctonic acid of hydrogenated cyclooctatetraene-maleic anhydride adduct (1.5 g.) was dissolved in tetrahydrofuran and esterfied with diazomethane as before to give 1.0 g. of ester. The ester was recrystallized twice from methanol to give a product of m.p. 167.8-168.8°. This ester had infrared absorption bands at 5.646 μ and 5.771 μ which are characteristic of carbonyl absorptions of γ-lactones and normal saturated esters, respectively.

Anal. Calcd. for $C_{13}H_{15}O_4Br$: C, 49.54; H, 4.8; Br, 25.35; Found: C, 49.45. 49.63; H, 4.80, 4.97; Br, 25.25.

Irradiation of Toluene and Maleic Anhydride.--Freshly distilled maleic anhydride (10.0 g., 0. 102 mole) was dissolved in 250 ml. of thiophene-free toluene and the solution was irradiated for 21 hours in the usual apparatus. The solution turned yellowish brown. After washing with four 75 ml. portions of water the toluene solution was distilled *in vacuo* on a steam bath to leave a pale yellow liquid residue. In order to isolate the product as an acid the pale yellow liquid was refluxed for one hour with 100 ml. of 2.5 N sodium hydroxide solution. The alkaline solution was acidified and extracted with ether several times and the ether solution was dried over anhydrous $MgSO_4$. On evaporating, the ether gave 5.0 g. of pale yellow syrupy liquid. A portion of this material (3.5 g.) was gently boiled on a steam bath with chloroform to precipitate 0.72 g. of a crystalline product of m.p. 157-158°. The chloroform solution was chromatographed on a silicic acid column using chloroform as eluent.

This procedure gave three fractions: 2.00 g. of a crystalline solid of m.p. 150-159°; 0.52 g. of liquid; and 0.23 g. of a glassy substance.

Irradiation of Toluene and Maleic Anhydride using Hydroquinone.-- Hydroquinone (1.0 g.) was added to a solution of 10 g. of maleic anhydride in 320 ml. of toluene. All the hydroquinone did not go into solution even after vigorous shaking. The undissolved portion was removed by filtration and the clear solution was irradiated for 21 hours. The solution was worked up as before to give 3.5 g. of crude liquid adduct.

In another case 50 ml. of acetone was added to a solution of 10.0 g. of maleic anhydride in 275 ml. of toluene with 1.0 g. of hydroquinone. This time all the hydroquinone went into solution. The clear solution was irradiated for 24 hours with nitrogen bubbling through the solution. The mixture was worked up as before to give 1.39 g. of product.

Esterification of Toluene-Maleic Anhydride Adduct.--The adduct was prepared as before using 10 g. of maleic anhydride and 320 ml. of toluene and irradiating the solution for 25 hours. The solution was extracted five times with 60 ml. portions of water and then the toluene was removed by distillation in vacuo on a steam bath to give 6.76 g. of a thick yellow liquid. The cell was washed three times with acetone and after evaporating the acetone washings another 3.0 g. of liquid product was obtained. The total yield of the adduct was 9.76 g.

The liquid adduct (9.76 g.) was heated at reflux for 25 hours with 130 ml. of 0.56 N potassium hydroxide. The alkaline solution was cooled and acidified with dilute hydrochloric acid and then extracted with ether several times. The ether solution was washed with water and dried over anhydrous $MgSO_4$. To this dry ether solution was added an ether solution

of diazomethane until a pale yellow color persisted. After standing for 2 hours the ether was removed by evaporation and the resulted pale yellow liquid was again dissolved in ether and washed with dilute sodium bicarbonate solution several times and finally with water and then dried over anhydrous $MgSO_4$. The ether was evaporated and the remaining pale yellow liquid was vacuum distilled at 0.15 mm. and a bath temperature of 141-160° to give 2.0 g. of a pale yellow liquid.

The vapor phase chromatograph was run on this ester at 196° or 249° on a Perkin-Elmer Vapor Fractometer Model 154 provided with a SE-30 column. The chromatogram showed only one sharp peak indicating that it contained only one component.

Saponification of Ester of Toluene-Maleic Anhydride Adduct.--The ester (1.0 g.) obtained above was refluxed for 3 hours with 100 ml. of 2.417 N potassium hydroxide. The solution was cooled and acidified with dilute hydrochloric acid to give a white crystalline precipitate which, after separation by filtration and drying, amounted to 0.9 g. of product of m.p. 158-160°. (Recorded[1] m.p. of benzylsuccinic acid 161-162°).

Irradiation of p-Xylene and Maleic Anhydride.--Freshly distilled maleic anhydride (10.0 g., 0.102 mole) was dissolved in 300 ml. of p-xylene and the solution was irradiated for 23 hours in the usual apparatus. The solution turned pale yellow but was clear. In order to remove any unconverted maleic anhydride the solution was washed five times with 60 ml. portions of water and then dried over anhydrous $MgSO_4$. The solvent was removed in vacuo with the aid of a steam bath, and the resulting syrupy liquid was cooled overnight in a refrigerator. It became a sticky solid which weighed 6.68 g.

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[1]See reference (51).

It had a characteristic odor and dissolved very readily in ether and acetone.

To the above sticky solid product was added n-hexane and the mixture was heated on a steam bath. Some of the product went into solution and a pale yellow oil remained. The n-hexane layer was separated and cooled to give 1.10 g. of a crystalline product of m.p. 85-87°. The weight of the oil was 5.56 g. A small amount of the solid portion was recrystallized from hot n-hexane and vacuum sublimed at 0.015 mm and bath temperature of 100° to give a compound of m.p. 86-87°.

Anal. Calcd. for $C_{12}H_{12}O_3$: C, 70.75; H, 5.92. Found: C, 69.72, 70.49; H, 5.88, 6.07.

Hydrolysis of the Solid Fraction from p-Xylene-Maleic Anhydride Adduct.--The solid fraction (0.4 g.) was heated at reflux with 25 ml. of 0.1 N sodium hydroxide for an hour. It was then acidified with dilute hydrochloric acid and extracted with ether. The ether solution was evaporated over anhydrous $MgSO_4$ to give a sticky solid which became crystalline on cooling in a refrigerator. It had a m.p. of 115-117.5°. (Recorded[1] m.p. for p-methylbenzylsuccinic acid 114-115°).

Esterfication of the Liquid Fraction from p-Xylene-Maleic Anhydride Adduct.--The liquid fraction (5.56 g.) was heated at reflux for one hour with 200 ml. of methanol saturated with dry hydrogen chloride. The solvent was removed by distillation on a steam bath and the resulting liquid was dissolved in ether and washed with dilute sodium bicarbonate solution several times and finally with water. After drying over anhy-

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[1] See references (51) and (52).

drous $MgSO_4$, the ether was removed by evaporation to give a yellow liquid with a characteristic odor. It was vacuum distilled at 0.05 mm. and a bath temperature of 190° to give 3.0 g. of a pale yellow liquid. Another distillation at 0.05 mm. and 160° did not remove the color of the liquid.

Saponification of Ester of p-Xylene-Maleic Anhydride Adduct.--The ester (1.0 g.) was heated at reflux for 21 hours with 100 ml. of 1 N sodium hydroxide. The mixture was then acidified with dilute hydrochloric acid and extracted with ether three times.. The ether solution was washed with water and dried over anhydrous $MgSO_4$. The solvent was removed by evaporation to give 0.8 g. of a thick liquid, which became crystalline on cooling in a refrigerator. This product had a m.p. of 113.5-114.0°. A small portion was recrystallized from hot n-hexane to give a white crystalline solid of m.p. 115-117°(recorded[1] m.p. for p-methylbenzylsuccinic acid 114-115°).

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[1]See references (51) and (52).

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